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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C09D 4/00</b>	<b>A2</b>	(11) International Publication Number: <b>WO 00/20517</b> (43) International Publication Date: <b>13 April 2000 (13.04.00)</b>
<p>(21) International Application Number: <b>PCT/NL00/00025</b></p> <p>(22) International Filing Date: <b>14 January 2000 (14.01.00)</b></p> <p>(30) Priority Data: <b>60/116,339</b>                      <b>19 January 1999 (19.01.99)</b>                      <b>US</b></p> <p>(71) Applicant (for all designated States except US): <b>DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).</b></p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): <b>CHAWLA, Chander, Prashash [IN/US]; 1300 North Avenue, Batavia, IL 60150 (US). NOREN, Gerry, Karl [US/US]; 721 Butterfield Drive, Algonquin, IL 60102 (US). KRONGAUZ, Vadim, Valerie [RU/US]; 1192 Foxboro Lane, Bartlett, IL 60103 (US). TRONCHE, Christopher [FR/US]; 731 Kemah Court, Schaumburg, IL 60193 (US). JARIA, Rajni [US/US]; Apartment 2B, 9124 Senate Drive, Des Plaines, IL 60016 (US). HA, Chau, Thi, Minh [VN/US]; 200 N Arlington Heights Road #607, Arlington Heights, IL 60004 (US). VANDEBERG, John, Thomas [US/US]; 503 Lake Shore Drive, Barrington, IL 60010 (US).</b></p>		<p>(74) Agent: <b>DEN HARTOG, Jeroen, Hendrikus, Joseph; DSM Patents &amp; Trademarks, P.O. Box 9, NL-6160 MA Geleen (NL).</b></p> <p>(81) Designated States: <b>AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b></p> <p><i>Upon the request of the applicant, before the expiration of the time limit referred to in Article 21(2)(a). Without international search report and to be republished upon receipt of that report. Without classification; title and abstract not checked by the International Searching Authority.</i></p>
<p>(54) Title: <b>RADIATION-CURABLE COMPOSITIONS COMPRISING MALEIMIDE COMPOUNDS AND METHOD FOR PRODUCING A SUBSTRATE WITH A CURED LAYER</b></p> <p>(57) Abstract</p> <p>The present invention relates generally to radiation-curable compositions comprising maleimide compounds and to methods of making and using the same. In particular, the present invention relates to radiation-curable compositions, comprising maleimide compounds, suitable for use in filled compositions as inks, coatings, hard coats, lacquers and/or adhesives for substrates such as plastic films, metal films, fiber optics, recordable media, compact discs (CD) and digital versatile discs (DVD), as well as in thin layer stereolithography or rapid prototyping applications.</p>		

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RADIATION-CURABLE COMPOSITIONS COMPRISING MALEIMIDE  
5 COMPOUNDS AND METHOD FOR PRODUCING A SUBSTRATE WITH A  
CURED LAYER

The invention relates generally to  
10 radiation-curable compositions comprising maleimide  
compounds, to a substrate with a cured coating, and to  
methods for producing the same. In particular, the  
present invention relates to radiation-curable  
compositions, comprising maleimide compounds, suitable  
15 for use in filled compositions as inks, coatings, hard  
coats, lacquers and/or adhesives for substrates such as  
plastic films, metal films, fiber optics, recordable  
media, compact discs (CD and CD-R), digital versatile  
discs (DVD), as well as thin layer stereolithographic  
20 or rapid prototyping applications.

BACKGROUND OF THE INVENTION

Numerous photoinitiators with varying  
structures are commercially available for use in  
25 different systems. However, nearly all commercially  
available radiation curing processes require a large  
percentage of these expensive initiators to be  
incorporated into the formulation. Many times the cost  
of the overall system is significantly impacted by the  
30 presence of these expensive initiators.

Although large percentages are required to  
achieve the desired cure rates, a relatively large

portion of the expensive photoinitiators added is not consumed or does not bind into the cured system. Indeed, the use of these conventional photoinitiators typically results in the production of small molecule photo-byproducts. The presence of the residual photo-active compounds or extractables result in degradation of the physical properties of the cured system, such as decreased color fastness, discoloration, and lower resistance to oxidative degradation. In addition, the residual photoinitiator and/or photo-byproducts lead to slow release of contaminants to the environment and contribute to long-term degradation in performance of the cured system.

Moreover, it is generally believed that thin coatings of conventional radiation-curable compositions do not cure well at low radiation dose levels because of an oxidation or oxygen inhibition effect. The oxygen inhibition effect most strongly effects coating surfaces that are exposed or were exposed to air or other oxygen rich environments for extended periods. It is believed that oxygen is absorbed into the coating which interferes with or prevents the curing of radiation-curable compositions using conventional photoinitiators, particularly at low radiation levels. The thinner the coating layer the more profound the oxygen inhibition effect, due to the high surface area to volume ratio which supports fast oxygen diffusion into the layer.

WO 98/07759 discusses a method for photopolymerizing and photopolymerizable compositions comprising maleimide compounds. In particular, this reference discusses the use of several mono- and multifunctional aliphatic maleimide compounds for the

photopolymerization of acrylates, in other words, as photoinitiating compounds. According to WO 98/07759, the photopolymerizable compositions comprise aliphatic amines as co-initiators to improve cure speed.

5           The disadvantage of such compositions is that they cure at lower rates and require higher dosages of energy to cure than compositions using conventional photoinitiators. For example, in WO 97/31981 150 micrometer thick layers of radiation-  
10 curable compositions comprising e.g. maleimide compounds are cured with a UV dose of 2 J/cm<sup>2</sup>, whereas in practice often less than 0.5 J/cm<sup>2</sup> is used.

#### Summary of the Invention

15           An object of the present invention is to provide a method for producing a coated substrate, and a radiation-curable composition that allows a high cure rate, in particular a cure rate comparable with conventional photoinitiated compositions. More in  
20 particular a curing rate such that at 0.5 J/cm<sup>2</sup> irradiation more than 85% of the ethylenically-unsaturated functional groups of the radiation-curable composition have reacted, preferably more than 90%, preferably, at the bottom as well as at the surface of  
25 the layer of the radiation-curable composition applied on the substrate.

          A further object of the present invention is to provide radiation-curable filled compositions, ink, coating, hard coat, lacquer and/or adhesive  
30 compositions comprising maleimide compounds, that are suitable for substrates such as plastic films, metal films, fiber optics (including coated fiber optics), recordable media (e.g., as a hardcoat), CD and CD-R

lacquers, DVD adhesives and/or thin layer stereolithographic or rapid prototyping applications.

Another object of the present invention is to provide a radiation-curable composition that  
5 minimizes and/or overcomes the effect of oxygen inhibition and achieves suitable surface and/or through cure particularly when applied in thin layers (i.e., 20  $\mu\text{m}$  or less, preferably 15  $\mu\text{m}$  or less).

The present invention relates to radiation-  
10 curable compositions comprising

- a) at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b), further called maleimide-free compound;
- 15 b) at least one aliphatic maleimide compound; and
- c) an aliphatic amine group comprising compound wherein component (c) is an amine functional acrylic polymer. Surprisingly, the amine functional acrylic polymer is very effective as amine synergist and the  
20 resulting composition shows a remarkably good cure speed. Moreover, said amines are non-extractable.

The invention also relates to a radiation curable ink composition for coloring coated optical glass fibers wherein the ink composition comprises  
25 a (meth)acrylate functional oligomer,  
a reactive diluent,  
a maleimide compound (b), and  
at least one pigment in an amount of about 1 to about 15 wt.%. Further, the invention relates to a  
30 radiation-curable DVD adhesive composition, to a radiation-curable CD or CD-R lacquer, to a substrate with a cured layer and to two substrates adhered to each other with a cured layer.

The invention relates to a coated optical fiber and to a ribbon or bundle of a plurality of coated optical fibers.

The present invention is thus directed to  
5 radiation-curable compositions comprising maleimide compounds, which can act as polymerization initiators. In contrast to conventional photoinitiators, substantially all of the maleimides are consumed during initiation and/or photopolymerization. Thus, the  
10 present invention can minimize or eliminate problems associated with the residue(s) resulting from the use of large percentages of conventional photoinitiators.

The invention further relates to a method for producing a substrate with a cured layer comprising  
15 the steps of:

(i) applying a radiation-curable composition to a substrate to form a layer on the substrate wherein the composition comprises

- 20 a) at least one maleimide-free compound having ethylenically unsaturated bonds, and
- b) at least one aliphatic maleimide compound;  
and

(ii) radiation-curing said layer with radiation of a wavelength between 200-800 nm, characterized in that  
25 the composition is applied in such a way that the layer before cure has a thickness of less than about 20 micrometer.

Preferably, said method for producing a substrate with a cured layer is used for at least one  
30 of the previously described applications and is not used for testing purposes.

In common applications, the surface that is at least partially coated and at least partially cured

is at least about 1 cm<sup>2</sup>, preferably at least about 2 cm<sup>2</sup>, more preferably at least about 3 cm<sup>2</sup>.

Preferably, the substrate is not a gold-coated aluminium plate.

5                   In another preferred embodiment the method for producing a substrate with a cured layer does not comprise a step, such as for example a pre-bake or post-bake step at higher temperatures, such as in the range of between 80 and 200°C.

10                   Optionally, the coating composition according to the present invention contains a non-reactive solvent. If the coating composition contains a non-reactive solvent, the layer according to the present invention can even be applied in a thickness  
15 greater than 20 micrometer, if - after evaporation of the non-reactive solvent - a layer before cure is obtained of less than about 20 micrometer. Preferably, the layer before cure has a thickness of between 1 and 19 micrometer, more preferably between 2 and 15  
20 micrometer, most preferred between 2 and 10 micrometer.

When aliphatic maleimides are used in compositions applied in said thin layers, the degree of cure is surprisingly good. Thus, surprisingly, a thickness effect has been observed when using maleimide  
25 compounds as photoinitiating compounds instead of or additionally to conventional photoinitiators. When using relatively low cure doses, maleimide containing layers having a thickness of greater than 20 µm (e.g. 100 µm) show insufficient bottom or through-cure  
30 whereas -surprisingly- when said layers are applied in a thickness of less than 20 µm, the through-cure is remarkably better.



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Furthermore, the invention relates to a method for producing a substrate with a cured layer wherein a radiation-curable composition comprising

- 5           a)     at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b), and
- (b)     at least one aliphatic maleimide compound,
- 10     is applied to a substrate to form a layer on the substrate that is sufficiently thin that said layer, when radiation-cured with an irradiation of  $0,125 \text{ J/cm}^2$ , is characterized by more than 85% reaction of the ethylenically unsaturated groups at the bottom and at the surface of said layer.

15           The bottom of said layer can be defined as that side of the layer which is located close to or against the substrate.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE  
PRESENT INVENTION

20

          Preferably, the radiation-curable composition of the present invention is applied in such a thickness that the layer after evaporation of non-reactive solvent, which optionally is present, and

25     before cure has a thickness of less than about 20 micrometer; preferably less than about 19 micrometer, more preferably less than about 15 micrometer, and particularly preferred less than about 10 micrometer. Typically, the thickness will be greater than about 1

30     micrometer, preferably greater than about 2 micrometer. Generally speaking, a coating can shrink between about 4 and about 8 % by curing. Hence, a cured coating will have a thickness of less than the original pre-coat

thickness. The term "original pre-coat thickness" relates to the thickness of the uncured coating as applied and after evaporation of non-reactive solvent, which optionally is present.

- 5                   The radiation-curable composition comprises
- a) at least one maleimide-free compound having ethylenically-unsaturated functionality and
  - b) at least one maleimide compound.

Both components a) and b) may include mixtures of  
10 compounds. Maleimide-free herein refers to compounds that do not include a maleimide moiety.

Examples of the ethylenically-unsaturated functional group in compounds of component (a) include (meth)acrylate, propenylether, vinylether, allylether,  
15 (substituted) styrene, N-vinyl, fumarate, maleate, itaconate, (meth)acrylamide, and mixtures of these. Preferred ethylenically-unsaturated functional groups are (meth)acrylate, N-vinyl, styrene and vinylether. Most preferred compounds for component (a) include  
20 (meth)acrylate functional compounds.

The term "acrylate(d)" as further used herein can be defined as acrylate(d) or as methacrylate(d).

Component (a) is preferably a mixture of  
25 oligomers and reactive diluents. Component (a) may be present in an amount of between 20 wt.% and 90 wt.%, preferably between 35 wt.% and 70 wt. %, more preferably between 40 wt.% and 65 wt. %. Also preferred is a mixture of monofunctional and multifunctional  
30 compounds. Examples of suitable oligomers comprise acrylated polyethers, acrylated polyesters, acrylated urethanes, acrylated epoxies, vinyl-ether functional urethanes and the like. For example, the acrylated

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urethanes can have polyether, polyester, polycarbonate, hydrocarbon backbones and the like.

The reactive diluents can be mono- or multi-functional. Examples of suitable reactive  
5 diluents are laurylacrylate, ethylacrylate, ethoxyethylacrylate, phenoxyethylacrylate, hexanedioldiacrylate, triethyleneglycol divinylether, trimethylol propanetriacrylate, isobornylacrylate, N-vinyl caprolactone, N-vinyl pyrrolidone,  
10 diethyleneglycol diacrylate, cyclohexyldimethanol diacrylate and the like.

In one embodiment of the invention, the radiation-curable composition comprises compounds having electron rich and electron poor double bonds, as  
15 described in EP-A-618237 and WO 97/31981, the entire disclosure of each are hereby incorporated by reference. The composition can comprise at least one ethylenically unsaturated compound having an electron donating group and at least one ethylenically  
20 unsaturated compound having an electron withdrawing group. In another preferred embodiment, the composition comprises only electron-poor double bonds such as (meth)acrylates, fumarate compounds, maleate compounds, maleimide compounds and the like.

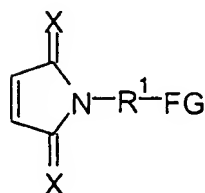
25 Surprisingly, the composition comprising only electron-poor double bonds and at least an aliphatic maleimide compound according to the present invention results in a remarkably good cure speed and achieves the objectives of the present invention.

30 The maleimide component b) includes aliphatic maleimides which includes maleimides wherein a non-aromatic group is attached to the nitrogen of the maleimide group. Suitable compounds include mono- and

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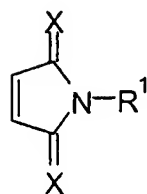
multifunctional maleimide compounds. Further suitable maleimide compounds are described in WO 98/07759 and WO 97/31981, the entire disclosure of each are hereby incorporated by reference.

- 5 Preferred maleimides include those which are represented by formula (1) or (2) as follows:



(1)

10



(2)

- wherein X independently represents an O or S atom,
- 15 wherein R¹ represents a carbon chain comprising at least one organic group like alkyl, alkanol, alkanon, alkyl-aryl wherein a non-aromatic saturated carbon chain is, attached to the nitrogen of the maleimide, and wherein FG represents a reactive functional group like amine,
- 20 hydroxy, acrylate, or a linking group like ester, carbonate, urea, urethane, ether and the like.
- R¹ may include 1, 2 or more carbon atoms. Generally, R¹ will comprise less than 20 carbon atoms, preferably less than 10. Preferably, R¹ is an aliphatic alkylene
- 25 group, more preferably, a straight chain alkylene, but

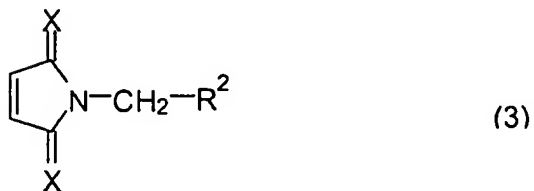
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it may comprise a cyclic group. One particularly preferred compound is cyclohexyl maleimide.

Preferably,  $R^1$  comprises 1 or 2 methylene carbon spacers, more preferred 1 methylene carbon spacer.

- 5 Compounds comprising two or more maleimide groups, further called multi-functional maleimide compounds, are very suitable as well.

In a preferred embodiment of the present invention, the maleimide compound comprises one or more  
10 groups according to formula (3)



15

wherein  $R^2$  is represented by one of the following

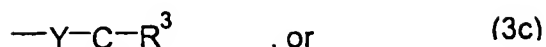


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25

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5

wherein

each X, independently, represent an O or S atom,

Y represents an O or S atom or an NH radical,

10 Z<sup>1</sup> and Z<sup>2</sup> independently represent an O or S atom or an NR<sup>5</sup> radical, and wherein R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> can independently represent a H atom or an organic radical.

In a preferred embodiment, the maleimide compound is a multifunctional maleimide compound. Such  
15 compound preferably is a compound according to formula (3) wherein R<sup>3</sup>, or at least R<sup>3</sup> or R<sup>4</sup> is the remainder of the backbone of a multifunctional maleimide compound.

The unsaturated bond of the maleimide preferably is unsubstituted. However, the maleimide may  
20 be substituted with one alkyl or aryl group with 1-6 carbon atoms. Hence, the unsaturated bond of the maleimide in the formulae of this application can be denoted as HC = CR<sup>4</sup> wherein R<sup>4</sup> represent a hydrogen atom or an alkyl or aryl group with 1-6 carbon atoms. If  
25 both R<sup>4</sup> groups are alkyl groups, the cure speed severely lowers or at least, the maleimide compound does not polymerize due to steric hinderance.

The molecular weight of the maleimide compound will generally be higher than 110 and  
30 preferably higher than 150. The molecular weight of the

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maleimide compound generally will be lower than about 100,000, although the upper limit is not critical, and will be mainly determined by viscosity limitations of the radiation-curable composition. Preferably, the molecular weight will be lower than about 50,000, more preferably, lower than about 10,000, and particularly preferred below about 5,000 because such molecular weights make it more easy to formulate radiation curable compositions without non-reactive diluents.

10 Molecular weight as used herein, unless otherwise specified, is (for oligomeric compounds) the number average molecular weight, as determined by GPC with polystyrene standards.

Multifunctional maleimide groups comprising compounds according to the invention and exemplified by formula (3) appear to be very efficient for the induction of photopolymerization of for example acrylates, even in the absence of any other photoinitiator.

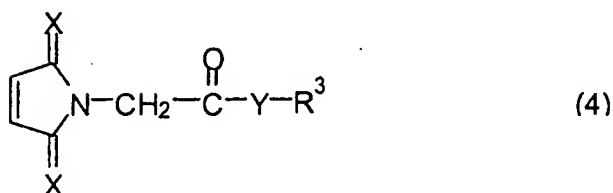
20 Preferably, the multifunctional maleimide compound has a functionality of 1.6 or higher, more preferably 1.9 or higher, in particular preferred 2.5 or higher, as a higher functionality appears to improve cure speed and to give cured products with lower photoinitiator based extractables.

The upper limit of the functionality seems to be non-critical, and the functionality will in general be lower than 20, preferably lower than 10 and in particular will be about 5 or lower.

30 The functional maleimide compound according to this invention preferably has a carbonate, urethane, ester, amine, amide, imide or ether as the functional group.

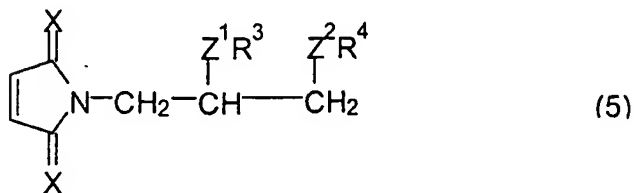
In one particularly preferred embodiment the maleimide groups are present as depicted in formula (4)

5



10 wherein Y is as defined above. Most preferably, Y represent an O atom or a NH radical, and R<sup>3</sup> is as defined above.

In another particularly preferred embodiment, the maleimide groups present may be  
15 represented by formula (5) as follows:



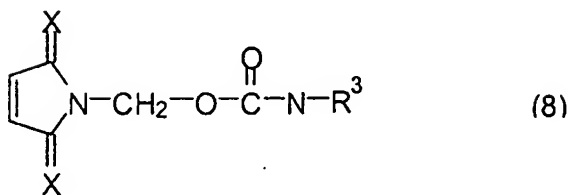
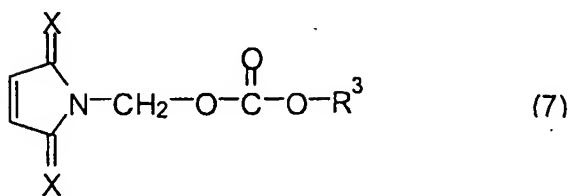
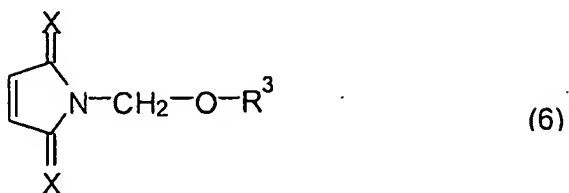
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wherein Z<sup>1</sup>, Z<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are as defined above. Preferably, either R<sup>3</sup> or R<sup>4</sup> represents a hydrogen atom and one of R<sup>3</sup> or R<sup>4</sup> is an organic group, being the  
25 remainder of the backbone of the maleimide compound.



Other preferred compounds include those represented by formulae (6)-(8) as follows:

5



10

The maleimide groups are attached via the functional group to a remainder of the molecule.

The R<sup>3</sup>-group can be any suitable organic molecule such as hydrocarbons, polyesters, polyethers, polycarbonates, polyurethanes, polyimides, polyamides, polyacrylates and the like.

This molecule can be of low or high molecular weight and can comprise ethylenically unsaturated groups.

Suitable molecules can be derived from

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hydroxy or amine functional molecules such as, for example, from cyclohexanol, butanol, triethylene glycol hexanediol, trimethylolpropane, pentaerythritol, dipentaerythritol, amine functional dendrimers like

5 Astramol®, polyethyleneglycol, polypropylene-glycol, amine functional polyesters, available as Jeffamine®, acid or hydroxyfunctional polyesters derived from diols, diacids and/or hydroxy acids, acid, amino or hydroxyfunctional acrylic polymers, isophorone

10 diisocyanate, toluene diisocyanate, and trimerization products therefrom, polycarbonate-diols, and the like.

For multifunctional compounds, preferred backbone molecules are polyethers, polycarbonates, polyesters, and acrylic polymers and most preferred

15 polyalcohols and polyethers such as ethoxylated or propoxylated trimethylol propane or trimethylolethane, (ethoxylated) pentaerithritol, pentaerithritol diacrylate (propoxylated) glycerol, polytetrahydrofuran, polyethylenoxide, polypropyleneoxide and the like.

20 Examples of suitable maleimide compounds include cyclohexylmaleimide, 2-ethylhexylmaleimide, n-butylmaleimide, laurylmaleimide, triethyleneglycol-biscarbonatebisethylmaleimide, 2-ethylcarbonate ethylmaleimide, 2-isopropylurethaneethyl maleimide, 2-

25 acryloylethylmaleimide, acetoxyethylmaleimide, isophoronebisurethane bisethylmaleimide, bisethylmaleimide carbonate, 4,9-dioxa-1,12 dodecane bismaleimide the reaction product of

N[(chloroformyl)methyl] maleimide with e.g. 1,6-

30 hexanediol, trimethylolpropane, pentaerythritol, tri- or tetraethylene glycol, polypropyleneglycol, polytetramethyleneglycol, hydroxy functional polyester,

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ethanol, n-butanol, t-butanol, monohydroxy functional polyethers, 4-hydroxybutylvinylether and the like. Preferably, cyclohexylmaleimide is used.

The maleimide compound preferably is  
5 present in the radiation-curable composition in an amount between 0.01-60 wt.%, preferably between 0.1-20 wt.%, more preferably between 0.2 and 10 wt.%.

The radiation-curable composition used in the method of the present invention comprises  
10 components (a) and (b); for purposes of definition of wt. amounts, the total amount of (a) + (b) is 100 wt.%, and additional compounds that can be present are defined relative to the amount of (a) + (b), unless otherwise specified.

15 The compositions comprising (a) and (b) are radiation-curable as such. Nevertheless, cure speed can be further improved by using conventional photoinitiators, preferably free-radical photoinitiators such as type I and type II  
20 photoinitiators. Examples of suitable type I (homolytic) photoinitiators are benzoin derivatives, methylolbenzoin and 4-benzoyl-1,3-dioxolane derivatives, benzilketals,  $\alpha,\alpha$ -dialkoxyacetophenones,  $\alpha$ -hydroxy alkylphenones,  $\alpha$ -aminalkylphenones,  
25 acylphosphine oxides, acylphosphine sulphides, halogenated acetophenone derivatives and the like. Commercial examples of suitable type I photoinitiators are Darocur 1173 (2-hydroxy-2-methyl-1-phenylpropane-1-one as the active component), Irgacure 184 (hydroxy-cyclohexyl phenyl ketone as the active component),  
30 Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), Irgacure 369 (2-benzyl-2-

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dimethylamino-1-(morpholinophenyl)-butan-1-one as the active component), acylphosphines such as Lucirin TPO (2,4,6-trimethylbenzoyl diphenyl phosphine oxide), Irgacure 819 (bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine- oxide). Also mixtures of type I  
5 photoinitiators can be used. For pigmented systems such as inks, Irgacure 907 is preferred.

Examples of suitable Type-II (hydrogen abstraction) photoinitiators aromatic ketones such as  
10 benzophenone, xanthone, derivatives of benzophenone, Michler's ketone, thioxanthone and other xanthone derivatives like ITX (isopropyl thioxanthone), anthraquinones, coumarine in an amount between 0.1-10 wt.%, preferably at least 2.0 wt.% (relative to (a) +  
15 (b)). Chemical derivatives and combinations of these photoinitiators can also be used.

Type-II photoinitiators generally are used with an amine synergist.

When using compound (b) according to the  
20 present invention, with or without the presence of a Type-II photoinitiator, amine synergists are not necessary, in particular if curing is performed under a nitrogen atmosphere. Hence, amine synergists (c) are preferably present in an amount of less than 1 wt.%,  
25 and more preferably less than 0.1 wt.%. If curing is performed under an oxygen containing atmosphere, like in air, an amine synergist (c) can be useful in amounts up to 10 wt.%, preferably in amounts between 0.1-5 wt.%.

30 Preferably, the amine synergist or amine compound (c) is chosen from the group consisting of a monomer tertiary amine compound, an oligomer (polymer) tertiary amine compound, a polymerizable amino acrylate

compound, a polymerized amino acrylate compound and mixtures thereof.

The amine-synergist may include tertiary amine compounds, such as alkanol-dialkylamines (e.g., ethanol-diethylamine), and ethylenically-unsaturated amine-functional compounds including amine-functional polymer compounds. The ethylenically-unsaturated amine compounds may also include dialkylaminoalkyl(meth)acrylates (e.g., diethylaminoethylacrylate) or N-morpholinoalkyl-(meth)acrylates (e.g., N-morpholinoethyl-acrylate). It appeared that in particular N-morpholino-ethylacrylate was a very efficient amine-synergist when used in combination with an aliphatic maleimide like cyclohexylmaleimide, and with a type II photoinitiator like benzophenone and optionally in the presence of an amine functional acrylic polymer as further described.

Suitable amine functional, ethylenically-unsaturated polymer compounds may include acrylated polymers. Such acrylated polymers may include the acrylated acrylic polymers such as those described in U.S. Patent 5,847,021 (Tortorello et al.), the entire disclosure of which is hereby incorporated by reference. It will be appreciated that these same amine functional, ethylenically-unsaturated polymer compounds, such as an acrylic polymer comprising an aliphatic amine functional group, may be suitable as at least one maleimide-free compound (a) of the compositions and be present in the amounts noted above for component (a), preferably in amounts between 35 and 70 wt.%. .

In particular, the acrylated acrylic polymer may include those formed by a vinyl addition

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copolymer formed by reacting at least one ethylenically-unsaturated, hydroxy functional copolymerizable monomer with at least one ethylenically-unsaturated, amine functional monomer. The amine functional monomer may include tertiary amines and/or aliphatic amines and preferably aliphatic tertiary amines. Suitable ethylenically-unsaturated, amine functional monomers include dialkylaminoalkyl(meth)acrylates such as diethylaminoethyl acrylate and/or morpholinoalkyl(meth)acrylates such as N-morpholinoethylacrylate. Preferably, the ethylenically-unsaturated polymer will comprise the vinyl addition, hydroxy and amine functional copolymer as a backbone with the ethylenically-unsaturated groups linked via urethane linkages. Most preferred is the amine functional acrylated acrylic polymer. These polymeric amine synergists appear to be very effective, and have the additional advantage that these amines are non-extractable, and are part of the ultimate network.

In one preferred embodiment of the present invention the radiation-curable composition comprises (a) at least one maleimide-free compound having ethylenically unsaturated bonds (b) a monofunctional aliphatic maleimide, (c) an amine functional acrylated acrylic polymer, and (d) a benzophenone compound.

Preferably, component (b) is cyclohexyl maleimide.

In another preferred embodiment of the present invention the radiation-curable composition comprises components (a)-(d) as described in the

previous preferred embodiment and additionally comprises a N-morpholino(meth)acrylate, more preferably N-morpholinoethylacrylate as an amine-synergist.

The radiation-curable composition

5 optionally comprises, in addition to components (a), (b) and the at least one amine synergist (c), a photoinitiator (d). These components are preferably present in amounts, relative to the total weight of (a) + (b) + (c) of:

10 component (b) 0.1-10 wt.%, component (c) 0.01-10 wt.%, more preferably 0.04-9.0 wt.% and component (d) 0.01-15 wt.%, more preferably 0.15-15 wt.%. Furthermore, it is preferred to use type II photoinitiators as component (d). And when the  
15 maleimide component includes alkylmaleimides, it is preferred to use a higher amount of type II photoinitiator than maleimide. Preferably, the type II photoinitiator is present in an amount of more than 2 wt.%.

20 The above amounts are in particular applicable if the compounds used have a relatively low molecular weight. Thus, if the amine forms part of a polymer, the amine group containing monomer with which the polymer is made will be present - in polymerized  
25 form - in 0.1-10 wt.%. Equally, if maleimide groups are part of a polymer, more than 10 wt.% of the maleimide comprising polymer can be used. The amounts can also be defined in terms of equivalent molar amounts, in concreto by the units meq of functional group per g of  
30 the formulation.  $C_4H_2NO_2$  is the functional group for the maleimide compound, benzophenone is taken as the functional group for the Type II photoinitiator, and for the amine functional compound dimethylamino is

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taken as the functional group. The amounts in equivalent molar amounts preferably will be 0.01 - 1.0 meq of maleimide groups per g of the formulation (more preferred 0.1-0.7 meq/g, particularly preferred, 0.1 to 5 0.5 meq/g); 0.01-0.8 meq of type II photoinitiating groups per g of the formulation (more preferred 0.05-0.6 meq/g, particularly preferred, 0.1 to 0.4 meq/g) and 0.01-2 meq/g of alkylamino groups per gram of the formulation (more preferred 0.1-1.5 meq/g, particularly 10 preferred 0.1 to 1.0 meq/g).

In systems where fast curing is desired, it may be preferred to include additional ethylenically-unsaturated components particularly those with labile hydrogens. Suitable compounds include alkoxyated 15 compounds, particularly alkoxyated monomers. These alkoxyated compounds may include ethoxyated and propoxyated compounds preferably having from 2-9 alkoxyated groups, for example, ethoxyated hexanedioldiacrylate, ethoxyated trimethylolpropane 20 triacrylate, ethoxyated bisphenol A dimethacrylate, ethoxyated nonyl phenol acrylate, propoxyated hexanedioldiacrylate, propoxyated trimethylolpropane triacrylate, propoxyated bisphenol A dimethacrylate, propoxyated nonyl phenol acrylate and propoxyated 25 glycerol triacrylate.

In many applications of these radiation-curable compositions it is desirable for the cured composition to be transparent, in other words, to be derived from a curable layer which is substantially 30 free of coloring agent. However, there are applications wherein it is desirable for the radiation-curable composition to include color, in other words, wherein the radiation-curable composition further comprises at



least one coloring agent. For these applications, which include ink coatings for identification of coated optical fibers, pigments and/or colorants are added to the radiation-curable composition. Suitable pigments or  
5 dyes are for example copper phthalocyanine blue, crystal violet lactone (blue), crystal malachite green, sheet fed rubine (red). The amount of pigment, if used, will in general be about 0.1 wt. % to about 10 wt.%, preferably between about 0.2 wt.% and about 5 wt.%  
10 relative to the coating composition.

The radiation-curable compositions can further comprise other additives, fillers and the like, such as for example flow agents, stabilizers, antioxidants, slip agents, waxes, dyes, wetting agents  
15 and the like.

The radiation-curable coating composition can be cured by different kinds of radiation, such as UV and EB radiation. The most preferred irradiation source is ultraviolet light. With respect to UV-curing  
20 equipment we refer to, for example, pages 161-234 of Chemistry and Technology of UV and EB-formulations, Volume 1, Oldring 1991. Suitable lamps employed to provide the desired high intensity and suitable wavelength and spectral distribution include for  
25 example those available from Fusion Systems, Corp. Preferably, H, D or excimer lamps are used.

It is preferred to formulate radiation-curable compositions that require less than about 0.5 J/cm<sup>2</sup> to achieve at least about 85 percent reacted  
30 acrylic unsaturation (% RAU), more preferably more than about 90% RAU. It is particularly preferred that the radiation-curable composition achieve such % RAU with about 0.3 J/cm<sup>2</sup> or less. Generally, an energy input of

at least about  $0.05 \text{ J/cm}^2$ , particularly of about  $0.1 \text{ J/cm}^2$  or more is required to achieve the desired cure.

The radiation-curable coating composition according to the invention can be used on different  
5 substrates, for example glass, paper, wood, plastic, brick, metals such as aluminum and iron. In particular, the radiation-curable composition of the present invention can be used as coatings for substrates such as plastic films, metal films, for fiber optics  
10 (including primary and secondary coatings, and/or inks), hard coat coatings for recordable media such as programmable cards (often referred to as "smart cards"), coatings for optical discs comprising a polymer substrate and a metallic reflective layer, and  
15 potentially further comprising at least one organic dye as a data recording medium. Examples are lacquers for CD's and CD-R's and adhesives for DVD's. A DVD can be described as comprising an adhesive composition and two optical discs adhered to one another by the adhesive  
20 composition wherein at least a portion of each disc which contacts the adhesive composition includes a radiation-cured adhesive provided by curing the radiation-curable adhesive composition. In other words, a DVD comprises two (optical discs) substrates adhered  
25 to each other with a radiation-cured adhesive or layer. These coating and/or adhesive layers are typically less than about 20 micrometer thick, preferably less than about 19 micrometer thick, more preferably less than about 15 micrometer and particularly preferred, less  
30 than about 10 micrometer thick.

The term 'optical fiber' as used herein can be defined as 'optical fiber' or as 'coated optical fiber'.

ExamplesExamples I-IV

Compositions suitable as ink layers for coloring coated optical glass fibers, or as thin protective layers, were prepared from constituents as described in Table 1. Amounts are given in parts by weight.

Compositions were tested as clear coatings of 5-7  $\mu\text{m}$  thickness and the % Reacted Acrylic Unsaturation (%RAU) was measured using real-time infrared spectroscopy. Further, pigmented compositions were prepared by adding pigments (3 parts by weight white  $\text{TiO}_2$  and 9 parts by weight blue  $\beta$ -copper (II) phthalocyanine to the clear base), and milling the resultant mixture till a homogeneous mixture was obtained. The composition was cured and the % RAU and MEK double rubs were measured, as well as adhesion to an outer primary optical fiber coating (Desolite 950-111®, available from DSM Desotech Inc.) and the release properties from a matrix optical fiber coating (Cablelite 950-706, available from DSM Desotech Inc.).

Table 1

Components	E X A M P L E S			
	I	II	III	IV
CN 966 J75 <sup>1)</sup>	22.4	22.4	-	-
SR 238 <sup>2)</sup>	23.0	-	23.0	-
Amino-oligomer A <sup>3)</sup>	35.1	35.1	57.5	57.5
RCC 13-361 <sup>4)</sup>	-	23.0	-	23.0
Ebecryl 350 <sup>5)</sup>	1	1	1	1
BHT <sup>6)</sup>	0.5	0.5	0.5	0.5
N-cyclohexylmaleimide	3.0	3.0	3.0	3.0
Benzophenone	3.0	3.0	3.0	3.0
Clear Coat				
% RAU (0.2 J/cm <sup>2</sup> )	98	99	94	97
% RAU (0.125 J/cm <sup>2</sup> )	98	99	92	95
Pigmented Ink				
% RAU (0.125 J/cm <sup>2</sup> )	91	94	94	95
MEK Rubs*	14	14	32	20
Adhesion to outer primary	Good	Good	Good	good
Release from matrix	Very slight zip	no zip	no zip	no zip

<sup>1)</sup> urethane acrylate in isobornylacrylate, obtainable from Sartomer

<sup>2)</sup> hexanedioldiacrylate from Sartomer

5 <sup>3)</sup> Amino group containing oligomer from synthesis A

<sup>4)</sup> ethoxylated hexanedioldiacrylate

<sup>5)</sup> silicon acrylate from UCB

<sup>6)</sup> butylated hydroxy toluene

\* the low number of MEK rubs is an inherent result for  
10 very thin films, even if the film is properly cured.

#### Synthesis A, preparation of an amino-oligomer A

An amine functional acrylic is formed by reacting 11 wt.% methyl methacrylate, 54 wt.% 2-  
15 ethylhexyl acrylate, 5 wt.% hydroxyethyl acrylate and 30 wt.% dimethylaminoethyl methacrylate in a polypropylene glycol diluent. The resulting acrylic copolymer had a Tg of -43.5°C and was present in the

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diluent at a 1:1 weight ratio.

A urethane acrylated acrylic was formed by reacting 43.0 wt.% of the above formed copolymer mixture, 24.19 wt.% isophorone diisocyanate, 12.63 wt.% hydroxyethyl acrylate, 20 wt.% isobornyl acrylate, 0.1 wt. % butylated hydroxy toluene (BHT) and 0.05 wt.% dibutyltindilaurate. The resulting urethane acrylated acrylic, herein referred to as Amino-oligomer A, had a viscosity ( $Z_4$  @  $10.3 \text{ s}^{-1}$  shear rate) of 343 Pa.s, a Gardner color value of 5-6 and an amine value of (meq/g) of 0.405.

#### Test Procedures:

15

%RAU - This is an FTIR method for determining the degree of cure on the surface of a coating to a depth of 1 to 3  $\mu\text{m}$ , following exposure to a predetermined dose of UV radiation. A drawdown of the sample material is first formed on a glass plate. The drawdown is then exposed to the predetermined dose of UV radiation to cure the drawdown and form a coating. The coating is cut into strips, approximately 10 mm by 50 mm.

25

An infrared spectrum of the uncured, liquid sample and an infrared spectrum of the cured sample are obtained. Infrared spectrometry is now well known and any infrared spectrometer can be utilized to obtain the infrared spectrum.

30

The net peak area of the acrylate unsaturation absorbance for the uncured liquid sample is measured. For most acrylate-based coatings, the absorbance at about  $810 \text{ cm}^{-1}$  should be used. However,

if the coating contains a siloxane or other component which absorbs strongly at or near  $810\text{ cm}^{-1}$ , an alternative acrylate absorbance peak can be used. The absorbances at about  $1410\text{ cm}^{-1}$  and about  $1635\text{ cm}^{-1}$  have  
5 been found to be satisfactory. The net peak area can be measured using the well known baseline technique in which a baseline is drawn tangent to absorbance minima on either side of the peak. The area above the baseline and under the peak is the net peak area.

10 A reference area is then determined. The reference absorbance should not change in intensity as the liquid sample is cured. Many formulations have an absorbance in the range of about 780 to about  $750\text{ cm}^{-1}$  that can be used as a reference absorbance. The net  
15 peak area of the reference absorbance is measured.

The ratio of the acrylate absorbance to the reference absorbance for the uncured, liquid sample is determined using the following formula:

20 
$$R_L = A_{AL} / A_{RL}$$

where

$A_{AL}$  is the net peak area of the acrylate absorbance,

$A_{RL}$  is the net peak area of the reference absorbance,

25 and

$R_L$  is the area ratio for the liquid sample.

The ratio of the acrylate absorbance to the reference absorbance for the cured sample is  
30 determined using the following formula:

$$R_C = A_{AC} / A_{RC}$$

where

$A_{AC}$  is the net peak area of the acrylate absorbance,

$A_{RC}$  is the net peak area of the reference absorbance,

and

5  $R_C$  is the area ratio for the cured sample.

The degree of cure as a percent reacted acrylate unsaturation (%RAU) is determined using the following formula:

10

$$\%RAU = [(R_L - R_C) \times 100\%] / R_L$$

MEK Rubs - A film of the pigmented composition was drawn on a black & white Brush Leneta Form 5DX using a  
15 #2.5 Meyer rod. The film was cured at 0.125 J/cm<sup>2</sup> under nitrogen using a Fusion "H" lamp. The cured film was tested using a cotton swab soaked in methylethylketone. The film was rubbed in a continuous back and forth motion, with one back and forth motion equal to 2  
20 single rubs. The number of rubs completed before the substrate is exposed is defined by the MEK rubs value.

Adhesion/Release of Inks - a sandwich structure consisting of an outer primary/an exemplary coating  
25 (which can be an ink) and a matrix, respectively, was prepared. A 3 mil thick film of a commercial outer primary coating was formed on Mylar and cured at 1.0 J/cm<sup>2</sup> under nitrogen using a Fusion "D" lamp. A film of one of the above examples was formed on the cured outer  
30 primary coating using a 6.35  $\mu$ m (0.25 mil) bird bar. This film layer was then cured at 0.35 J/cm<sup>2</sup> under nitrogen using a "H" lamp. A 76.2  $\mu$ m (3 mil) thick film

layer of a commercial matrix composition was then drawn on top using a 7.52 cm (3 inch) square bar and cured at 1.0 J/cm<sup>2</sup> under nitrogen using a "D" lamp. This sandwich composite was cut into 1.27 cm (0.5 inch) wide strips  
5 and the adhesion to the outer primary coating and release of the matrix were observed by separating the matrix layer and peeling it from the ink layer at a 45° angle. Adhesion to the outer primary coating is measured as either "good" or "bad" and the release from  
10 the matrix material is evaluated by the sound made during release with a "zipper" sound indicating poor release and no sound or "no zip" indicating good release.

15 Examples V-VII

Compositions were prepared from constituents as shown in Table 2A. The described compositions are useful as outer primary coatings or as matrix materials. Curing was achieved by irradiation  
20 with an H-lamp in nitrogen atmosphere. All compositions were measured, after cure, for percentage reacted acrylic unsaturation (% RAU) both at the top surface and bottom surface of the coating layer and the results are shown in Table 2B.



Table 2A

Components	E X A M P L E S		
	V	VI	VII
Amino Functional Urethane Acrylate (A)	50	--	--
Amino oligomer (B)	--	30	30
Ethoxylated (6) trimethylolpropane triacrylate	33.5	50	50
Ethoxylated hexanediol diacrylate	--	6	6
Isobornyl acrylate	12.5	6	6
Dimethylamine ethyl acrylate	--	0.5	1.83
Cyclohexyl maleimide	2	7	1.83
Benzophenone	2	0.5	4.34

Table 2B

Properties	E X A M P L E S		
	V	VI	VII
Film thickness 6 $\mu\text{m}$ , cure at 125 mJ/cm <sup>2</sup>			
% RAU Top	87	-	-
% RAU Bottom	91	-	-
Film thickness 12.5 $\mu\text{m}$ , cure at 125 mJ/cm <sup>2</sup>			
% RAU Top	88	88	93
% RAU Bottom	90	48*	91
Film thickness 25 $\mu\text{m}$ , cure at 125 mJ/cm <sup>2</sup>			
% RAU Top	89	82	93
% RAU Bottom	88	58*	92
Film thickness 50 $\mu\text{m}$ , cure at 125 mJ/cm <sup>2</sup>			
% RAU Top	90	73	93
% RAU Bottom	84	24*	82
Film thickness 75 $\mu\text{m}$ , cure at 125 mJ/cm <sup>2</sup>			
% RAU Top	89	69	93
% RAU Bottom	84	10*	76
Film thickness 6 $\mu\text{m}$ , cure at 500 mJ/cm <sup>2</sup>			
% RAU Top	92	95	97
% RAU Bottom	93	97	97
Film thickness 12.5 $\mu\text{m}$ , cure at 500 mJ/cm <sup>2</sup>			
% RAU Top	93	95	97
% RAU Bottom	93	98	96
Film thickness 25 $\mu\text{m}$ , cure at 500 mJ/cm <sup>2</sup>			
% RAU Top	93	96	97
% RAU Bottom	94	97	96
Film thickness 50 $\mu\text{m}$ , cure at 500 mJ/cm <sup>2</sup>			
% RAU Top	95	96	98
% RAU Bottom	93	94	96
Film thickness 75 $\mu\text{m}$ , cure at 500 mJ/cm <sup>2</sup>			
% RAU Top	96	97	98
% RAU Bottom	93	86	96

\* insufficient cure

At dosage of 0.5 J/cm<sup>2</sup> and above, all  
 5 coatings were cured regardless of thickness, which  
 ranged from between 6  $\mu\text{m}$  and 75  $\mu\text{m}$ . However, at a dose  
 of 0.125 J/cm<sup>2</sup> only the thin coatings were fully cured  
 while the bottom surface of the thick coatings were not  
 sufficiently cured. When using conventional

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photoinitiators like Darocure 1173 or Lucirin TPO, this behavior was not observed (i.e., all coatings were fully cured with  $0.125 \text{ J/cm}^2$  irradiation irrespective of a thickness).

5                   Therefore, it has surprisingly been found that there exists an effect of layer thickness on the degree of cure (through-cure and surface cure) when using maleimide compounds as photoinitiating compounds, the effect being such that the thinner the layer the  
10   better the degree of cure (especially visible under conditions of lower cure doses). The critical layer thickness at which at least 85% RAU is obtained at a cure dose of  $0.5 \text{ J/cm}^2$  is dependent on the specific composition (Ex. V-VII).

15

Synthesis B, preparation of an amino-oligomer B

                  An amine functional acrylic is formed by reacting 25 wt.% methyl methacrylate, 60 wt.% 2-ethylhexyl acrylate, 5 wt.% hydroxyethyl acrylate and  
20   10 wt.% dimethylaminoethyl methacrylate in a polypropylene glycol diluent. The resulting acrylic copolymer had a Tg of  $-41^\circ\text{C}$  and was present in the diluent at a 50.7:49.3 weight ratio.

                  A urethane acrylated acrylic was formed by  
25   reacting 43.24 wt.% of the above formed copolymer mixture, 24.07 wt.% isophorone diisocyanate, 12.57 wt.% hydroxyethyl acrylate, 20 wt.% isobornyl acrylate, 0.1 wt. % butylated hydroxy toluene (BHT) and 0.02 wt.% dibutyltindilaurate. The resulting urethane acrylated  
30   acrylic, herein referred to as Amino-oligomer B, had a viscosity ( $Z_4 @ 10.3\text{s}^{-1}$ ) of 540 Pa.s, a Gardner color value of 4-5 and an amine value of (meq/g) of 0.136.

Examples VIII-XVII

Radiation-curable compositions were prepared from constituents as shown in Tables 3(A-C). The described compositions are useful as CD lacquers including recordable-CD (r-CD) lacquers. The CD-lacquer generally has a thickness between about 4 and about 12 micrometer. The composition in Table 3B & C were inspected to determine extent of curing.

10 Preparation of Base CompositionTable 3A

<u>Composition</u>	<u>Base Composition</u>
CD540 <sup>1</sup>	26.4
Ebecryl 53 <sup>2</sup>	23.6
Tetraethylene glycol diacrylate (Sartomer)	31.4
Tetrahydrofurfuryl acrylate (Sartomer)	8.99
CN-112C60 <sup>3</sup>	8.99
LG-99, an acrylic oligomer (Estron)	0.56
Hydroquinone monomethyl ether	0.06

Table notes:

- 1<sup>1</sup>) ethoxylated (4) bisphenol A dimethacrylate  
 15 2<sup>2</sup>) propoxylated glycerol triacrylate  
 3<sup>3</sup>) 40% Epoxy Novolak acrylate/60% Trimethylolpropane triacrylate

Radiation-curable CompositionTable 3B

	XIII	IX
Components (wt.% of total composition)		
Base Composition	87	83
Cyclohexyl maleimide	5	8
Ethyl diethanol amine (EDEA)	3	4
Darocur 1173 <sup>1</sup>	5	5
0.5 J/cm <sup>2</sup> (H bulb)		
Outer edge	4	4
Inner cure	3	5
Surface cure	5	5

5 Table notes:

<sup>1</sup>) 2-hydroxy-2-methyl-1-phenylpropane-1-one as the active component (type I photoinitiator)

In Table 3B, the coating compositions were tested by applying the coating composition (approximately 0.5 g) to the central metallized area of the CD and spun to 4,000 rpm for 3 seconds (acceleration of 3500 rpm<sup>2</sup>). The coated CD's were then cured under air at a dose as indicated using a Fusion unit equipped with either a "D" or "H" bulb, as indicated. After exposing the coating, the coating was evaluated on the surface: i) at the central metallized region near the spindle (at a radius of about 25 mm), referred to as the "inner cure" (thickness of the coating is between about 4 and about 10  $\mu$ m, and ii) at a medial position along the surface (at a radius between about 39 and about 54 mm), referred to as the "surface cure" (thickness of coating is between about 7 and about 15  $\mu$ m); and along the "outer edge" of the CD.

Typically, the inner cure represents a region where the coating is the thinnest (due to centrifugal force) and is generally the more difficult area to achieve satisfactory curing. The "outer edge" stands for the degree of cure at the side of the CD. The coating is usually very thin here, can be partially spinned over the edge of the CD, and is usually difficult to cure. The requirement of having a good cure at the outer edge of the CD is only a practical one, for the purpose of not having several CD's stuck together during handling.

The extent of cure was determined by rubbing the coated area, after exposure, with a Kimwipes and visually inspecting the surface for smears. A scale of smearing was assigned, where "5" is indicative of complete surface cure (no smearing) and "0" was indicative of no cure (extensive smearing), with "4" and above considered an acceptable cure.

Table 3C

Example		X
Components (wt.% of total composition)		
Base Composition		86
Cyclohexyl maleimide		8
Ethyl diethanol amine (EDEA)		4
Isopropyl thioxanthone <sup>1)</sup>		2
PROPERTIES		
75 $\mu$ m	% Rau Top	87.1
	% Rau Bottom	80.3
50 $\mu$ m	% Rau Top	86.7
	% Rau Bottom	49.2
25 $\mu$ m	% Rau Top	86.3
	% Rau Bottom	80.3
12.5 $\mu$ m	% Rau Top	86.8
	% Rau Bottom	88.6

## Table notes:

<sup>1)</sup> type II (Hydrogen abstraction) photoinitiator

A drawdown of each material to be tested  
5 was prepared by drawing down a coating on a glass plate  
at the specified thickness, using a Bird bar,  
commercially available from Pacific Scientific, Silver  
Spring, MD. The drawdown coating was dosed with 0.5  
J/cm<sup>2</sup> of radiation in air using a "H" lamp from Fusion  
10 Curing Systems, Rockville, MD.

The thickness effect is clearly visible in the % Rau  
Top and particularly in the % Rau Bottom when going  
from a 50 micrometer to a 12.5 micrometer thick film.

15 Example XI

Radiation-curable compositions were  
prepared from constituents as shown in Table 4. The  
described compositions are useful as CD lacquers (and  
recordable media hardcoats). Curing was achieved by  
20 irradiation with a H lamp in air at different UV-doses.

The coating thickness as defined under  
Table 3B are applicable.

Table 4

	XI
CD540 <sup>1</sup>	22.5
Ebecryl 53 <sup>2</sup>	21
Tetraethylene glycol diacrylate (Sartomer)	23.7
Tetrahydrofurfuryl acrylate (Sartomer)	8
CN-112C60 <sup>3</sup>	8
LG-99; acrylic oligomer (Estron)	0.5
Hydroquinone monomethyl ether	0.05
Cyclohexyl maleimide	5
ethyl diethanol amine	3
Darocure 1173 <sup>1</sup>	5
PROPERTIES	
0.3 J/cm <sup>2</sup>	
Outer edge	5
Inner cure	4
Surface cure	5
0.5 J/cm <sup>2</sup>	
Outer edge	5
Inner cure	5
Surface cure	5
1.0 J/cm <sup>2</sup>	
Outer edge	5
Inner cure	5
Surface cure	5

Table notes:

- 5    <sup>1)</sup> ethoxylated (4) bisphenol A dimethacrylate  
       <sup>2)</sup> propoxylated glycerol triacrylate  
       <sup>3)</sup> 40% Epoxy Novolak acrylate/60% Trimethylolpropane triacrylate

#### 10    Examples XII-XIII

Radiation-curable compositions were prepared from constituents as shown in Table 5. The described compositions are useful as DVD adhesives. Curing was achieved by irradiation with a D-lamp at 1



J/cm<sup>2</sup> in air. The DVD-adhesive generally has a thickness between about 10 and about 75  $\mu$ m.

The DVD-adhesives of Ex. XII and XIII have a thickness of about 25  $\mu$ m.

5

Table 5

	XII	XIII
Components		
oligomer <sup>1)</sup>	46.5	21.95
Hexanedioldiacrylate	--	18.4
Isobornyl acrylate	36.75	--
4-hydroxybutyl acrylate	9.5	32
Bisphenol A dimethylacrylate	--	19.4
A-189 <sup>2)</sup>	1	1
Dimethyl acrylamide	3.0	1
Irganox 1035	0.25	0.25
Cyclohexylmaleimide	1.5	1.5
N-methyldiethanol amine	1.5	1.5
Benzophenone	3	3

Table notes:

<sup>1)</sup> poly THF urethane diacrylate

<sup>2)</sup> trimethoxypropyl mercapto silane

10

Examples XIV-XV

Radiation-curable compositions were prepared from constituents as shown in Table 6. The described compositions are useful as DVD adhesives.

15 Curing was achieved by irradiation with a D-lamp at 1 J/cm<sup>2</sup> in air.

Table 6

	XIV	XV
Components		
98-521 <sup>1)</sup>	46.5	41.51
Hexanedioldiacrylate	--	--
Isobornyl acrylate	36.75	32.82
4-hydroxybutyl acrylate	9.5	8.48
Bisphenol A dimethylacrylate	--	--
A-189 <sup>2)</sup>	1	0.9
Irganox 1035	0.25	0.22
Cyclohexymaleimide	1.5	5.35
Dimethylamine ethyl acrylate	--	8.92
N-methyldiethanol amine	1.5	--
Benzophenone	3	1.8

Table notes:

1) poly THF urethane diacrylate

2) trimethoxypropyl mercapto silane

C L A I M S

1. Method for producing a substrate with a cured layer comprising the steps of
  - 5 (i) applying a radiation-curable composition to a substrate to form a layer on the substrate wherein the composition comprises
    - a) at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b), and
    - 10 b) at least one aliphatic maleimide compound, and
  - (ii) radiation-curing said layer with radiation of a wavelength between 200-800 nm, characterized in that the composition is applied in such a way, that the layer before cure has a thickness of less than about 20 micrometer.
- 20 2. Method for producing a substrate with a cured layer according to claim 1, wherein the aliphatic maleimide compound b) is a multifunctional compound having on average at least 1.6 maleimide groups with at least one methylene carbon spacer between the maleimide chromophore and a functional group, attached to a backbone.
- 25 3. Method for producing a substrate with a cured layer according to claim 1, wherein the aliphatic maleimide compound b) is a monofunctional compound.
- 30 4. Method for producing a substrate with a cured layer according to claim 3, wherein the aliphatic maleimide compound b) is cyclohexyl maleimide.

5. Method for producing a substrate with a cured layer according to any one of claims 1-4, wherein the composition further comprises at least one amine compound (c) chosen from the group  
5 consisting of a monomer tertiary amine compound, an oligomer (polymer) tertiary amine compound, a polymerizable amino acrylate compound, a polymerized amino acrylate compound and mixtures thereof.
- 10 6. Method for producing a substrate with a cured layer according to any one of claims 1-5, wherein the composition further comprises a conventional photoinitiator.
7. Method for producing a substrate with a cured  
15 layer according to claim 6, wherein the conventional photoinitiator comprises a type II photoinitiator.
8. Method for producing a substrate with a cured layer according to any one of claims 1-7, wherein  
20 the ethylenically unsaturated compound is a (meth)acrylate compound.
9. Method for producing a substrate with a cured layer according to any one of claims 1-8, wherein the composition comprises at least one  
25 ethylenically unsaturated compound having an electron donating group and at least one ethylenically unsaturated compound having an electron withdrawing group.
10. Method for producing a substrate with a cured  
30 layer according to any one of claims 1-9, wherein the layer of the composition before cure has a thickness between 2 and 10 micrometer .
11. Method for producing a substrate with a cured

layer according to any one of claims 1-10,  
wherein the layer is substantially free of  
coloring agent.

12. Method for producing a substrate with a cured  
5 layer according to any one of claims 1-10,  
wherein the layer further comprises at least one  
coloring agent.
13. Method for producing a substrate with a cured  
layer according to any one of claims 1-12,  
10 wherein the composition is formulated to be a  
coating composition.
14. Method for producing a substrate with a cured  
layer according to any one of claims 1-12,  
wherein the composition is formulated to be an  
15 adhesive.
15. Method for producing a substrate with a cured  
layer according to any one of claims 1-14,  
wherein the substrate is glass, plastic, metal,  
wood, paper or brick.
- 20 16. Method for producing a substrate with a cured  
layer according to claim 14, wherein the method  
further comprises the step of applying a second  
substrate to the layer of a radiation-curable  
composition and radiation-curing said layer.
- 25 17. Method for producing a substrate with a cured  
layer according to any one of claims 1-16,  
wherein the layer is cured with a dose of 0.5  
J/cm<sup>2</sup> or less, to obtain a cured layer with more  
than 85% reacted unsaturation.
- 30 18. Method for producing a substrate with a cured  
layer wherein a radiation-curable composition  
comprising  
a) at least one compound having ethylenically

- unsaturated bonds other than those in maleimide groups as defined under (b), and (b) at least one aliphatic maleimide compound, is applied to a substrate to form a layer on the substrate that is sufficiently thin that said layer, when radiation-cured with an irradiation of  $0,125 \text{ J/cm}^2$ , is characterized by more than 85% reaction of the ethylenically unsaturated groups at the bottom and at the surface of said layer.
- 10 19. Substrate with a cured layer obtainable by the method according to any one of claim 1-18.
20. Substrate with a cured layer obtainable by the method according to claim 19, wherein the cured layer is between about 1 and about 20 micrometer thick.
- 15 21. Substrate with a cured layer according to any one of claims 19-20 wherein the substrate is a coated optical fiber and the cured layer is an ink or a colored coating.
- 20 22. Substrate with a cured layer according to any one of claims 19-20 wherein the substrate is an optical disc comprising a polymer substrate and a metallic reflective layer.
- 25 23. Substrate with a cured layer according to claim 22 wherein the optical disc further comprises at least one organic dye as a data recording medium.
24. A DVD comprising two substrates adhered to each other with a radiation-cured layer obtainable by the method according to claim 16.
- 30 25. A radiation curable composition comprising
- a) at least one compound having ethylenically unsaturated bonds other than those in

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- maleimide groups as defined under (b),
- b) at least one aliphatic maleimide compound,  
and
- c) an aliphatic amine group comprising  
5 compound
- wherein component (c) is an amine functional  
acrylic polymer.
26. Composition according to claim 25, wherein the  
polymer (c) comprises urethane groups and  
10 ethylenic unsaturated groups.
27. Composition according to any one of claims 25-26,  
wherein component (b) is a monofunctional  
aliphatic maleimide, component (c) is an amino-  
functional acrylated acrylic polymer and wherein  
15 the composition further comprises a benzophenone  
compound as component (d).
28. Composition according to any one of claim 25-27,  
wherein component (b) is cyclohexyl maleimide.
29. Composition according to claim 28 wherein the  
20 composition further comprises a N-morpholino  
alkyl(meth)acrylate.
30. Coated optical fiber comprising  
an optical fiber, coated with  
an inner primary coating composition, and with  
25 an outer primary coating composition and  
optionally with a colored ink layer applied  
thereon wherein at least one of the coating  
compositions or the optional ink layer comprises  
a maleimide compound (b).
- 30 31. Ribbon or bundle of a plurality of coated optical  
fibers with a matrix or bundling material wherein  
the matrix material or bundling material  
comprises a maleimide compound (b).

32. Radiation curable ink composition for coloring coated optical glass fibers wherein the ink composition comprises  
a (meth)acrylate functional oligomer,  
5 a reactive diluent,  
a maleimide compound (b), and  
at least one pigment in an amount of about 1 to about 15 wt.%.  
33. Ink composition for coloring coated optical  
10 fibers wherein the ink composition comprises the radiation curable composition according to any one of claims 25-29 and at least one pigment in an amount of about 1 to about 15 wt.%.  
15 34. Radiation curable digital versatile disc adhesive composition according to any one of claims 25-29.  
35. Radiation curable CD or CD-R lacquer comprising a radiation curable composition according to any one of claims 25-29.